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| In re the application of: | Attorney Docket No.: 2950.20US01 |
| Chaloner-Gill et al. | Confirmation No.: 2942 |
| Application No.: 09/845,985 | Examiner: Mark Ruthkosky |
| Filed: April 30, 2001 | Group Art Unit: 1745 |

For: PHOSPHATE POWDER COMPOSITIONS AND METHODS FOR FORMING PARTICLES WITH COMPLEX ANIONS

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DECLARATION UNDER 37 C.F.R. § 1.132

Mail Stop Amendments
Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

Sir:

I, Craig R. Horne, Ph.D., hereby declare as follows:

1.      I am presently CEO of EnerVault Inc., an early stage energy storage company.  I was awarded my Ph.D. in Materials Science & Mineral Engineering from the University of California, Berkeley in 2000.  I have nine published technical papers, have been active in the Electrochemical Society and have refereed papers for the Journal of the Electrochemical Society. I am presently an occasional consultant to the assignee, NanoGram Corp., on matters relating to battery technology.  I have been an employee or consultant to NanoGram, its parent company NeoPhotonics or its majority owned subsidiary Kainos Energy Corporation since I departed school at UC Berkeley in 1998.  I am an inventor on 15 issued U.S. Patents and numerous U.S. and foreign pending applications.  More details on my qualifications are found on the attached resume.   Dr. Horne has an equity interest in NanoGram Corp., but has no other specific pecuniary interest in the present application.

1

2.      I am an inventor on the patent application noted above that is presently under examination. I am familiar with the pending claims.

3.      I have carefully read U.S. patent 5,538,814 to Kamauchi et al. (Kamauchi), U.S. patent 5,789,115 to Manev et al. (Manev), and U.S. patent 5,910,382 to Goodenough et al. (Goodenough).

4.      I worked with Dr. On Chang to reproduce the formation of lithium cobalt phosphate and lithium iron phosphate based on the teachings of the Kamauchi patent. Specifically, we followed a procedure similar to the procedure of Example 1 of the Kamauchi patent. The details of this procedure are summarized in detail in my Declaration with Dr. Chang filed on April 6, 2006, which had an attached report.

5.      The as synthesized phosphate powders were processed using ball milling. The Kamauchi patent does not describe their milling techniques in detail. However, Example 7 at column 18 describes ball milling as a suitable milling approach. Similarly, Example 10 describes milling in a ball mill for 24 hours. This is the approach that we adopted for processing of the phosphate powders. A commercial ball mill was used, and the powders were milled for 24 hours. During the course of our work, we consulted with commercial milling companies and mill product suppliers. It was our belief that our milling approach was state of the art milling as of the filing date of the present application, April 30, 2001. The results of our phosphate particle processing were described in detail in the attaches report entitled "Grinding of Lithium Cobalt Phosphate Mixed Phase Material (Li-Co-PO$_4$) and Lithium Iron Phosphate (LiFePO$_4$)," which was attached to the Horne-Chang Declaration of April 6, 2006, and a copy of which is also attached to this Declaration.

6.      I have read the relevant parts of the Board of Appeal Decision of December 19, 2008 and the Decision on Request for Rehearing of July 14, 2009.

7.      To summarize the results of the grinding experiment, the ground phosphate powders were evaluated using both visual evaluation of scanning electron micrographs (SEM) and light

scattering of powders dispersed in a liquid. Transmission electron micrographs were not obtained since these would not have been meaningful beyond the SEM photos due to the large particles in the samples and the large range of particle sizes. The non-uniformity of the powders is readily observable in the SEM photographs, which clearly show tiny particles as well as relatively large chunks. These results are consistent with the light scattering results, which clearly show a very broad distribution of particle sizes.

Plots in the attached report show the particle size distribution by volume as well as by particle number for the two phosphate samples. The light scattering results were performed with an ultrasonic probe to break agglomerates. This state of the art dispersion approach should be very effective at separating particles within agglomerates. The light scattering measurements were performed by an independent contractor proficient in the measurement technique based on samples that we provided. In my experience, light scattering will result in a narrower distribution than a TEM analysis for at least two reasons. First, there is small particle drop out in the light scattering measurements, so the small diameter part of the distribution is under represented or absent, Also, agglomeration tends to involve more smaller particles so that you bias the distribution toward the middle.

8.    To facilitate the understanding of the results by the Patent Office, I am providing additional comments and interpretations of the results.

9.    The functional property most valuable to an active electrode material in a lithium battery is the specific energy. A material's specific energy is defined as the product of its insertion potential, measured in Volts, and its specific capacity, measured in mAh per unit weight of material (most commonly as mAh/g). The insertion potential is a property that is intrinsic to a given material composition as it relates to its underlying electronic structure. However, the specific capacity will depend markedly on the quality of the material. Therefore, for a given composition of active insertion electrode material (e.g. $LiFePO_4$), the specific capacity of a sample fabricated by a given process provides the most useful comparative value to assess its quality to the quality of a sample fabricated by a different process.

The specific capacity is a gravimetric function as it is normalized to unit mass. Therefore, as is the case with mass, the capacity of a particle relates to its volume and therefore,

the cube of its diameter. This means that if Particle 2 is twice the size of Particle 1, Particle 2 will have eight times the capacity of Particle 1. Accordingly, though a small number of large particles within a given collection does not significantly impact the size distribution, they will have a dramatic impact on the distribution as it relates to the material property of interest, capacity. Therefore, when evaluating the impact of a given fraction of particles outside a range of interest within a collection of active insertion electrode materials for lithium batteries, the percentage with respect to the mass (e.g. cube of the size or calculated volume) is the governing parameter to consider.

A comparison of the distributions calculated on a number % and mass % is presented below. Referring to Table A, the number % data are from Columns B1 and C1 for Li-Co-PO$_4$ and LiFePO$_4$, respectively, while the mass% data are from Columns E3 and F3 for Li-Co-PO$_4$ and LiFePO$_4$, respectively.
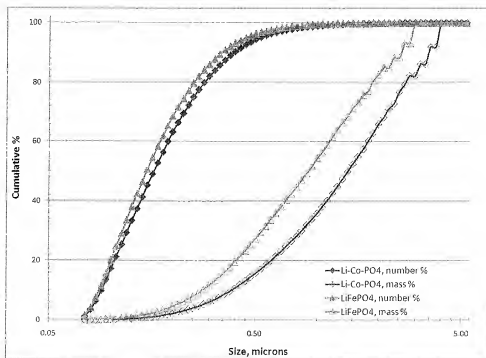


10. To obtain the average particle size, conventional analysis is used. An average is defined as the sum of the values divided by the number of values. When using a normalized distribution, the equivalent of the number of values is equal to 1. The numerator becomes the sum of the product of the probability times the diameter value. In other words, the average diameter $d_{ave}$ is calculated as follows: $d_{ave} = \Sigma \, d \cdot p_d$, where d is the diameter and $p_d$ is the weighted probably.

Referring then to Tables 5 and 6 in the Report, the diameter is given in one column and the probability is the difference in a percentage value in the second column minus the previous percentage value in the table divided by 100 to remove the percentage value. Table A, presented at the end of this Declaration, shows the average diameter calculated in this manner for Li-Co-$PO_4$ (cols. B1 to B3_ and $LiFePO_4$ (cols. C1 to C3). Columns A and B1 comprise of the data of Table 5 in the Report while Columns A and C1 are of Table 6. The probability of each diameter being present in a sample is calculated in Columns B2 and C2 while Columns B3 and C3 give the product of the diameter and probability. Therefore, the sum of Columns B3 and C3, given at the bottom, provide the average particle size of each sample based on the data provided in the Report.

As mentioned above, the cumulative mass fraction distribution is the governing parameter to consider when determining the impact of particle size on the functional properties of active insertion electrode materials for lithium batteries. Column D in Table A is the cube of the size given in column A and therefore represents the volume of a specific measurement channel. Columns E1 and F1 use the observation probability data of Columns B2 and C2 along with the densities for Li-Co-$PO_4$ and $LiFePO_4$, respectively[1], to calculate the mass of particles associated with each measurement interval (Columns A and D). The total sum of Columns E1 and F1 are used to calculate the mass % probability shown in Columns E2 and F2. Finally, the data in Columns E2 and F2 are used to calculate the cumulative mass % distributions given in Columns E3 and F3 for Li-Co-$PO_4$ and $LiFePO_4$, respectively.

Based on this analysis, the average diameter for Li-Co-$PO_4$ is 0.225 microns, and the average diameter for $LiFePO_4$ is 0.200 microns (data shown in Table A).

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[1] . Densities of Li-Co-$PO_4$ is taken as that of $LiCoPO_4$. Densities of both $LiCoPO_4$ and $LiFePO_4$ found in Table A were taken from J. Chen et al., Solid State Ionics **178**(2006)1676-1693.

| sample | mean size, μm | 5x mean size, μm | number % greater than 5x mean size | number % less than 0.40x and greater than 1.6x mean size | mass % greater than 5x mean size | mass % less than 0.40x and greater than 1.6x mean size |
|---|---|---|---|---|---|---|
| Li-Co-PO$_4$ | 0.225 | 1.125 | 0.73 | 22.33 | 59.7 | 91.4 |
| LiFePO$_4$ | 0.200 | 1.000 | 0.50 | 16.39 | 45.6 | 87.0 |

Table B. Calculated arithmetic mean size, 5x mean size, and % greater than 5x mean size (from data in Tables 5 and 6 of Report for Li-Co-PO$_4$ and LiFePO$_4$, respectively).

11.     Table B above shows that for Li-Co-PO$_4$, 5 times the average diameter is 1.125 microns. Referring to Table A, col. B1 (also given in Table 5 of the Report), about 0.73 percent of the particles have a size greater than 5 times the average particle size, as denoted by the bold red type. As specified in claim 1, essentially no particles have a size greater then 5 times the average size. Therefore, the ground materials fail to come close to this claimed feature. The impact of this failure is illuminated by Table A, col. E3. Since the material capacity is a gravimetric function (mAh/g), more than 59% of the total mass in given sample of particles is comprised of particles whose mass is 5x the mean.

12.     Table B above shows that for LiFePO$_4$, 5 times the average diameter is 1.000 microns. Referring to Table A, col. C1 (also given in Table 6 of the Report), about 0.50 percent of the particles have a size greater than 5 times the average particle size, as denoted by the bold red type. As specified in claim 1, essentially no particles have a size greater then 5 times the average size. Therefore, the ground materials fail to come close to this claimed feature. The impact of this failure is illuminated by Table A, col. F3. Since the material capacity is a gravimetric function (mAh/g), more than 45% of the total mass in given sample of particles is comprised of particles whose mass is 5x the mean.

13.     Referring to Table A, column B1 (also Table 5 in the Report), our claim 55 specifies that no more than 5% of the particles have a size less than 40 percent of the average particle size and greater than 160 percent of the average particle size. From the distribution in Table A, column B1 (also Table 5 in the Report), about 10% of the particles have a diameter less than 40% of the average (0.090 microns), as denoted by bold magenta type, and about 12.5% of the particles have

a particle size greater than 160% of the average particle size (0.360 microns), as denoted by bold orange type. Therefore, more than 22% of the particles falling outside this size range. Therefore, the uniformity obtained by milling also fell very short of the uniformity claimed in claim 55 of our application. The impact of this failure is illuminated by Table A, col. E3. Since the material capacity is a gravimetric function (mAh/g), more than 93% of the total mass in given sample of particles fall outside the specified range.

14. Referring to Table A, column C1 (also Table 6 in the Report), our claim 55 specifies that no more than 5% of the particles have a size less than 40 percent of the average particle size and greater than 160 percent of the average particle size. From the distribution in Table A, column C1 (also Table 6 in the Report), about 4% of the particles have a diameter less than 40% of the average (0.080 microns), as denoted by bold magenta type, and about 12% of the particles have a particle size greater than 160% of the average particle size (0.320 microns), as denoted by bold orange type. Therefore, more than 16% of the particles falling outside this size range. Therefore, the uniformity obtained by milling also fell very short of the uniformity claimed in claim 55 of our application. The impact of this failure is illuminated by Table A, col. F3. Since the material capacity is a gravimetric function (mAh/g), almost 92% of the total mass in given sample of particles fall outside the specified range.

15. Based on my extensive personal experience processing these types of materials and personal discussions with service providers, the milling of inorganic materials to produce specific results is relatively unpredictable. In general, milling for submicron materials is not expected to yield uniform materials, although new milling techniques under present development may improve on this circumstance when the technologies become more mature. Based on this generally known understanding, a person of ordinary skill in the art reading the Manev patent would have no expectation that milling of the Kamauchi materials would be successful to form the claimed highly uniform phosphate particles.

16. In summary, our experimental results confirm the expectations of a person of ordinary skill in the art that milling is simply incapable for producing uniform materials as disclosed and claimed in our patent application. Milling was not close to achieving the properties of the

claimed materials. These particle size measurements clearly demonstrate that conventional grinding approaches cannot produce phosphate powders with close to the uniformity of the phosphate powders claimed in the pending claims of the present application.

17.    I declare that all statements made herein that are of my own knowledge are true and that all statements that are made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

_____9/22/2009_____
Date

_____
Craig R. Horne, Ph.D.

CERTIFICATE OF ELECTRONIC TRANSMISSION

I hereby certify that this paper is being transmitted electronically to the U.S. Patent and Trademark Office on the date shown below.

September 22, 2009_____
Date

/Peter S. Dardi/_____
Peter S. Dardi, Ph.D., Reg. #39,650

8

Table A. Particle size data reductions showing cumulative number % and number % and calculated arithmetic mean size (columns B and C) and corresponding mass %, and cumulative mass % (columns E and F) for Li-Co-PO₄ and LiFePO₄ from data in Report tables 5 and 6, respectively.

| col.A | col.B1 | col.B2 | col.B3 | col.C1 | col.C2 | col.C3 | col.D | col.E1 | col.E2 | col.E3 | col.F1 | col.F2 | col.F3 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | Li-Co-PO₄ | | | LiFePO₄ | | | | Li-Co-PO₄ | | | LiFePO₄ | |
| size channel, µm | Cumulative number % (from Table 5) | number % | weighted size for channel | Cumulative number % (from Table 6) | number % | weighted size for channel | calculated volume channel, µm³ | density = 3.252 g/cc — mass in range, µg | mass % | cumulative mass % | density = 3.6 g/cc — mass in range, µg | mass % | cumulative mass % |
| 0.075 | 1.33 | 1.33 | 9.98E-04 | 1.57 | 1.57 | 1.18E-03 | 0.00022 | 1.34E-09 | 0.00707 | 0.00707 | 1.23E-09 | 0.01666 | 0.0167 |
| 0.080 | 3.60 | 2.27 | 1.82E-03 | 4.24 | 2.67 | 2.14E-03 | 0.00027 | 2.37E-09 | 0.0148 | 0.0227 | 2.33E-09 | 0.0344 | 0.0511 |
| 0.085 | 6.52 | 2.92 | 2.48E-03 | 7.65 | 3.41 | 2.90E-03 | 0.00033 | 3.65E-09 | 0.0226 | 0.0449 | 3.95E-09 | 0.0527 | 0.104 |
| 0.090 | 9.88 | 3.36 | 3.02E-03 | 11.57 | 3.92 | 3.53E-03 | 0.00038 | 4.99E-09 | 0.0308 | 0.0751 | 5.39E-09 | 0.0718 | 0.176 |
| 0.093 | 13.54 | 3.66 | 3.40E-03 | 15.79 | 4.22 | 4.01E-03 | 0.00045 | 6.96E-09 | 0.0395 | 0.115 | 6.33E-09 | 0.0950 | 0.267 |
| 0.100 | 17.39 | 3.85 | 3.85E-03 | 20.29 | 4.41 | 4.41E-03 | 0.00052 | 7.85E-09 | 0.0485 | 0.163 | 8.33E-09 | 0.1109 | 0.378 |
| 0.106 | 21.36 | 3.97 | 4.21E-03 | 24.70 | 4.50 | 4.77E-03 | 0.00062 | 9.64E-09 | 0.0595 | 0.223 | 1.01E-08 | 0.1348 | 0.512 |
| 0.113 | 23.39 | 4.05 | 4.55E-03 | 29.12 | 4.52 | 5.11E-03 | 0.00076 | 1.18E-08 | 0.0752 | 0.298 | 1.23E-08 | 0.1641 | 0.676 |
| 0.120 | 27.41 | 4.28 | 4.82E-03 | 33.70 | 4.48 | 5.39E-03 | 0.00088 | 1.39E-08 | 0.0859 | 0.382 | 1.43E-08 | 0.1999 | 0.866 |
| 0.126 | 31.41 | 4.00 | 5.10E-03 | 38.11 | 4.33 | 5.75E-03 | 0.00105 | 1.66E-08 | 0.1020 | 0.484 | 1.67E-08 | 0.2234 | 1.09 |
| 0.134 | 37.31 | 3.97 | 5.59E-03 | 42.45 | 4.33 | 5.80E-03 | 0.00120 | 1.85E-08 | 0.114 | 0.614 | 1.97E-08 | 0.321 | 1.33 |
| 0.142 | 41.48 | 4.01 | 5.64E-03 | 46.66 | 4.21 | 5.98E-03 | 0.00150 | 2.32E-08 | 0.143 | 0.749 | 2.28E-08 | 0.305 | 1.65 |
| 0.150 | 45.37 | 3.89 | 5.84E-03 | 50.74 | 4.08 | 6.12E-03 | 0.00177 | 2.68E-08 | 0.165 | 0.914 | 2.86E-08 | 0.346 | 2.00 |
| 0.159 | 49.13 | 3.81 | 6.06E-03 | 54.67 | 3.93 | 6.23E-03 | 0.00110 | 5.12E-08 | 0.193 | 1.11 | 5.43E-08 | 0.397 | 2.40 |
| 0.169 | 52.89 | 3.71 | 6.27E-03 | 58.44 | 3.77 | 6.37E-03 | 0.00300 | 3.65E-08 | 0.226 | 1.35 | 5.91E-08 | 0.458 | 2.86 |
| 0.179 | 56.49 | 3.60 | 6.44E-03 | 62.05 | 3.61 | 6.46E-03 | 0.00353 | 4.21E-08 | 0.260 | 1.59 | 5.43E-08 | 0.521 | 3.38 |
| 0.190 | 58.95 | 3.47 | 6.56E-03 | 65.47 | 3.42 | 6.48E-03 | 0.00423 | 4.77E-08 | 0.295 | 1.89 | 4.91E-08 | 0.561 | 3.96 |
| 0.200 | 63.39 | 3.13 | 6.96E-03 | 68.72 | 3.25 | 6.49E-03 | 0.00429 | 5.27E-08 | 0.333 | 2.22 | 5.90E-08 | 0.654 | 4.61 |
| 0.212 | 66.47 | 3.08 | 6.74E-03 | 71.78 | 3.06 | 6.46E-03 | 0.00429 | 5.17E-08 | 0.382 | 2.61 | 6.17E-08 | 0.623 | 5.35 |
| 0.225 | 69.50 | 3.05 | 6.93E-03 | 74.65 | 2.87 | 6.46E-03 | 0.00596 | 7.05E-08 | 0.435 | 3.04 | 6.17E-08 | 0.623 | 6.17 |
| 0.238 | 72.36 | 2.86 | 6.81E-03 | 77.32 | 2.67 | 6.35E-03 | 0.00706 | 7.86E-08 | 0.488 | 3.53 | 6.79E-08 | 0.906 | 7.07 |
| 0.252 | 75.05 | 2.69 | 6.70E-03 | 79.80 | 2.48 | 6.25E-03 | 0.00883 | 8.77E-08 | 0.542 | 4.07 | 7.49E-08 | 0.993 | 8.07 |
| 0.267 | 77.57 | 2.52 | 6.73E-03 | 82.10 | 2.30 | 6.14E-03 | 0.00900 | 9.77E-08 | 0.604 | 4.67 | 2.26E-08 | 1.501 | 9.17 |
| 0.283 | 79.91 | 2.34 | 6.62E-03 | 84.20 | 2.10 | 5.94E-03 | 0.0119 | 1.02E-07 | 0.668 | 5.34 | 8.98E-08 | 1.597 | 10.4 |
| 0.300 | 82.08 | 2.17 | 6.52E-03 | 86.11 | 1.91 | 5.73E-03 | 0.0141 | 1.19E-07 | 0.738 | 6.08 | 9.75E-08 | 1.57 | 11.7 |
| 0.318 | 84.07 | 1.98 | 6.51E-03 | 88.09 | 1.74 | 5.53E-03 | 0.0166 | 1.41E-07 | 0.906 | 6.91 | 1.06E-07 | 1.103 | 13.00 |
| 0.337 | 86.57 | 1.81 | 6.51E-03 | 89.50 | 1.57 | 5.28E-03 | 0.0199 | 1.75E-07 | 1.080 | 7.95 | 1.15E-07 | 1.498 | 14.6 |
| 0.358 | 87.55 | 1.56 | 5.91E-03 | 91.04 | 1.40 | 5.63E-03 | 0.0236 | 1.86E-07 | 1.153 | 9.08 | 1.15E-07 | 1.638 | 16.2 |
| 0.379 | 89.65 | 1.50 | 5.67E-03 | 92.06 | 1.02 | 4.31E-03 | 0.0336 | 1.97E-07 | 1.220 | 10.3 | 1.26E-07 | 1.727 | 17.9 |
| 0.400 | 90.39 | 1.34 | 5.56E-03 | 93.17 | 1.11 | 4.44E-03 | 0.0335 | 2.07E-07 | 1.28 | 11.9 | 1.44E-07 | 1.860 | 19.6 |
| 0.424 | 91.59 | 1.20 | 5.09E-03 | 94.14 | 0.97 | 4.11E-03 | 0.0399 | 2.15E-07 | 1.33 | 13.2 | 1.46E-07 | 1.915 | 21.5 |
| 0.449 | 92.66 | 1.07 | 4.30E-03 | 94.90 | 0.04 | 3.77E-03 | 0.0473 | 2.08E-07 | 1.33 | 14.4 | 1.51E-07 | 2.00 | 23.4 |
| 0.475 | 93.61 | 0.95 | 4.51E-03 | 95.72 | 0.74 | 3.51E-03 | 0.0561 | 2.15E-07 | 1.39 | 15.8 | 1.50E-07 | 2.05 | 25.4 |
| 0.503 | 94.14 | 0.83 | 4.17E-03 | 96.36 | 0.64 | 3.22E-03 | 0.0666 | 2.15E-07 | 1.33 | 17.1 | 1.54E-07 | 2.05 | 27.5 |
| 0.535 | 95.17 | 0.73 | 3.89E-03 | 96.90 | 0.54 | 2.88E-03 | 0.0793 | 2.15E-07 | 1.39 | 17.1 | 1.34E-07 | 2.56 | 29.5 |

| col. A size channel μm | col. B1 Cumulative number % (from Table 5) | col. B2 number % | col. #3 weighed size for channel | col. C1 Cumulative number % (from Table 6) | col. C2 number % LiFePO₄ | col. C3 weighted size for channel | col. D calculated volume channel, μm³ | col. E1 mass in range, μg | col. E2 mass % (density = 3.882 g/cc) | col. E3 cumulative mass % | col. F1 mass in range, μg (center = 3.882) | col. F2 LiFePO₄ mass % | col. F3 cumulative mass % |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 0.565 | 85.81 | 0.64 | 3.61E-03 | 97.37 | 0.47 | 2.66E-03 | 0.0944 | 2.95E-05 | 1.45 | 13.6 | 1.60E-07 | 2.13 | 51.6 |
| 0.599 | 86.36 | 0.55 | 3.29E-03 | 97.77 | 0.40 | 2.39E-03 | 0.112 | 2.40E-05 | 1.48 | 20.1 | 1.61E-07 | 2.15 | 53.8 |
| 0.634 | 86.85 | 0.49 | 3.11E-03 | 98.11 | 0.34 | 2.16E-03 | 0.133 | 2.54E-05 | 1.57 | 21.7 | 1.64E-07 | 2.18 | 56.0 |
| 0.671 | 87.27 | 0.42 | 2.82E-03 | 98.40 | 0.29 | 1.95E-03 | 0.158 | 2.54E-05 | 1.60 | 23.3 | 1.65E-07 | 2.20 | 58.2 |
| 0.711 | 87.63 | 0.36 | 2.56E-03 | 98.65 | 0.25 | 1.78E-03 | 0.188 | 2.73E-05 | 1.63 | 24.9 | 1.70E-07 | 2.26 | 60.4 |
| 0.753 | 87.95 | 0.31 | 2.41E-03 | 98.86 | 0.21 | 1.59E-03 | 0.214 | 2.73E-05 | 1.72 | 26.6 | 1.69E-07 | 2.26 | 42.7 |
| 0.798 | 88.22 | 0.27 | 2.13E-03 | 99.03 | 0.17 | 1.36E-03 | 0.266 | 2.80E-05 | 1.73 | 28.4 | 1.65E-07 | 2.27 | 44.9 |
| 0.845 | 88.45 | 0.23 | 1.95E-03 | 99.19 | 0.16 | 1.36E-03 | 0.316 | 3.13E-05 | 1.82 | 30.2 | 1.71E-07 | 2.27 | 47.1 |
| 0.895 | 88.57 | 0.18 | 1.62E-03 | 99.31 | 0.13 | 1.16E-03 | 0.375 | 5.51E-05 | 1.90 | 32.1 | 1.77E-07 | 2.34 | 49.5 |
| 0.948 | 88.85 | 0.16 | 1.62E-03 | 99.42 | 0.10 | 1.04E-03 | 0.446 | 5.44E-05 | 1.98 | 34.0 | 1.77E-07 | 2.35 | 51.8 |
| 1.005 | 89.01 | 0.14 | 1.49E-03 | 99.52 | 0.070 | 7.43E-04 | 0.531 | 5.51E-05 | 2.05 | 36.1 | 1.59E-07 | 2.12 | 54.4 |
| 1.064 | 89.15 | 0.12 | 1.35E-03 | 99.59 | 0.070 | 7.43E-04 | 0.631 | 5.16E-05 | 2.16 | 38.2 | 1.93E-07 | 2.52 | 56.5 |
| 1.127 | 89.27 | 0.11 | 1.31E-03 | 99.66 | 0.060 | 7.16E-04 | 0.749 | 3.50E-05 | 2.29 | 40.3 | 1.89E-07 | 2.57 | 59.0 |
| 1.194 | 89.36 | 0.090 | 1.14E-03 | 99.72 | 0.050 | 6.32E-04 | 0.891 | 3.71E-05 | 2.42 | 42.7 | 1.93E-07 | 2.55 | 61.6 |
| 1.265 | 89.43 | 0.070 | 9.35E-04 | 99.77 | 0.050 | 6.32E-04 | 1.060 | 3.71E-05 | 2.53 | 45.0 | 1.01E-07 | 2.42 | 66.8 |
| 1.340 | 89.50 | 0.070 | 9.02E-04 | 99.81 | 0.040 | 5.31E-04 | 1.260 | 5.92E-05 | 2.57 | 47.4 | 1.02E-07 | 2.43 | 64.7 |
| 1.419 | 89.63 | 0.050 | 7.86E-04 | 99.84 | 0.030 | 3.86E-04 | 1.496 | 4.15E-05 | 2.54 | 49.9 | 1.82E-07 | 2.56 | 71.3 |
| 1.503 | 89.66 | 0.050 | 6.74E-04 | 99.87 | 0.030 | 3.08E-04 | 1.775 | 4.15E-05 | 2.41 | 52.5 | 1.81E-07 | 2.05 | 73.5 |
| 1.592 | 89.73 | 0.040 | 7.14E-04 | 99.89 | 0.020 | 3.10E-04 | 2.113 | 4.64E-05 | 2.56 | 55.0 | 1.31E-07 | 2.41 | 75.7 |
| 1.686 | 89.77 | 0.040 | 6.01E-04 | 99.91 | 0.020 | 3.07E-04 | 2.509 | 4.14E-05 | 2.41 | 57.5 | 1.31E-07 | 2.03 | 73.7 |
| 1.786 | 89.81 | 0.030 | 4.25E-04 | 99.92 | 0.020 | 3.78E-04 | 2.983 | 6.55E-05 | 2.87 | 60.3 | 1.00E-07 | 1.48 | 77.2 |
| 1.892 | 89.84 | 0.030 | 4.50E-04 | 99.94 | 0.010 | 2.00E-04 | 3.546 | 5.16E-05 | 3.04 | 63.0 | 2.98E-07 | 3.41 | 80.6 |
| 2.004 | 89.87 | 0.030 | 6.01E-04 | 99.95 | 0.010 | 2.00E-04 | 4.214 | 4.92E-05 | 2.41 | 63.9 | 1.51E-07 | 2.02 | 82.6 |
| 2.123 | 89.88 | 0.020 | 4.25E-04 | 99.96 | 0.010 | 2.12E-04 | 5.010 | 5.90E-05 | 1.87 | 65.3 | 2.96E-07 | 2.41 | 85.0 |
| 2.249 | 89.93 | 0.020 | 4.50E-04 | 99.97 | 0.010 | 1.28E-04 | 5.956 | 6.58E-05 | 1.70 | 68.1 | 1.01E-07 | 0.00 | 83.6 |
| 2.382 | 89.94 | 0.010 | 2.50E-04 | 99.97 | 0.010 | 1.38E-04 | 7.077 | 7.55E-05 | 2.86 | 73.2 | 0.00E+00 | 0.00 | 88.4 |
| 2.523 | 89.95 | 0.010 | 2.83E-04 | 99.98 | 0.010 | 3.00E-04 | 8.409 | 5.58E-05 | 4.05 | 76.9 | 3.55E-07 | 4.80 | 93.2 |
| 2.673 | 89.95 | 0.010 | 2.67E-04 | 99.98 | 0.013 | 2.67E-04 | 10.006 | 8.39E-05 | 2.41 | 79.3 | 3.55E-07 | 0.00 | 95.1 |
| 2.831 | 89.96 | 0.010 | 2.83E-04 | 99.99 | 0.010 | 3.00E-04 | 11.820 | 4.82E-05 | 2.86 | 83.2 | 5.68E-07 | 6.79 | 100.0 |
| 2.999 | 89.96 | 0.010 | 0.00E+00 | 99.99 | 0.010 | 3.00E-04 | 14.123 | 4.82E-05 | 0.00 | 82.2 | 0.00E+00 | 0.00 | 100.0 |
| 3.177 | 89.97 | 0.010 | 3.18E-04 | 99.99 | 0.000 | 0.00E+00 | 16.790 | 6.55E-05 | 4.04 | 86.1 | 5.09E-07 | 0.00 | 100.0 |
| 3.365 | 89.97 | 0.000 | 4.25E-04 | 99.99 | 0.000 | 0.00E+00 | 19.931 | 0.00E+00 | 0.00 | 86.1 | 0.00E+00 | 0.00 | 100.0 |
| 3.565 | 89.98 | 0.000 | 5.05E-04 | 99.99 | 0.000 | 0.00E+00 | 23.703 | 3.70E-05 | 3.70 | 89.9 | 0.00E+00 | 0.00 | 100.0 |
| 3.776 | 89.99 | 0.000 | 0.00E+00 | 99.99 | 0.000 | 0.00E+00 | 28.190 | 9.95E-05 | 8.95 | 100.0 | 0.00E+00 | 0.00 | 100.0 |
| 3.999 | 89.99 | 0.000 | 4.00E-04 | 99.99 | 0.000 | 0.00E+00 | 33.483 | 1.30E-05 | 0.00 | 100.0 | 0.00E+00 | 0.00 | 100.0 |
| 4.235 | 89.99 | 0.000 | 0.00E+00 | 99.99 | 0.000 | 0.00E+00 | 39.790 | 0.00E+00 | 0.00 | 100.0 | 0.00E+00 | 0.00 | 100.0 |
| 4.487 | 89.99 | 0.000 | 0.00E+00 | 99.99 | 0.000 | 0.00E+00 | 47.301 | 0.00E+00 | 0.00 | 100.0 | 0.00E+00 | 0.00 | 100.0 |
| 4.753 | 89.99 | 0.000 | 0.00E+00 | 99.99 | 0.000 | 0.00E+00 | 56.221 | 0.00E+00 | 0.00 | 100.0 | 0.00E+00 | 0.00 | 100.0 |
| 5.035 | 89.99 | 0.000 | 0.00E+00 | 99.99 | 0.000 | 0.00E+00 | 66.834 | 0.00E+00 | 0.00 | 100.0 | 0.00E+00 | 0.00 | 100.0 |
| 5.333 | 89.99 | 0.000 | 0.00E+00 | 99.99 | 0.000 | 0.00E+00 | 79.417 | 0.00E+00 | 0.00 | 100.0 | 0.00E+00 | 0.00 | 100.0 |
| 5.650 | 89.99 | 0.000 | 0.00E+00 | 99.99 | 0.000 | 0.00E+00 | 94.397 | 0.00E+00 | 0.00 | 100.0 | 0.00E+00 | 0.00 | 100.0 |
| 5.984 | 100.00 | 0.000 | 5.99E-04 | 100.00 | 0.020 | 5.99E-04 | 112.437 | 1.37E-04 | n/a | 100.0 | 3.44E-06 | n/a | n/a |

average size: 0.225 μm    0.280 μm    total mass 123,799    total mass    1.624E-05 μg (per 10,000 particles)    7.505E-04 μg (per 10,000 particles)

# Grinding of Lithium Cobalt Phosphate Mixed Phase Material (Li-Co-PO$_4$) and Lithium Iron Phosphate (LiFePO$_4$)

On Chang and Craig Horne

NanoGram Corporation

## BACKGROUND

The purpose of this experiment is to evaluate the particle size distribution of metal phosphate nanoscale particles produced by following the teaching of U.S. Patent 5,538,814, the Kamauchi patent. For completeness, this demonstration was performed on two separate metal phosphate systems: (a) the Li-Co-PO$_4$ mixed-phase material that is the specific example in the Kamauchi patent, and (b) LiFePO$_4$.

## EXPERIMENTAL

### Chemicals

Cobalt (II) carbonate hydrated: Sigma-Aldrich, Cat. No. 202193, Lot No. 05130JC
Lithium carbonate: Sigma-Aldrich, Cat. No. 255823, 99% ACS grade, Lot No. 08004KC
Phosphoric acid: Ashland chemical, 85%, semiconductor grade
Iron (II) Oxide: Sigma-Aldrich, Cat. No. 400866, 99.9%, Lot No. 13722PC

### Equipment

Jar mill: One-tier jar high-capacity laboratory jar mill, 13" roller, Cole Parmer, Cat. No. EW-04149-00
Milling jar: HDPE milling jar, 0.25 gal, with ridges on the interior to improve tumbling of the grinding media. Cole Parmer Cal. No. EW-04172-02
Milling jar sleeve: Milling jar sleeve, Cole Parmer Cat. No. EW-04172-12
Grinding media: Zirconia grinding media, 3/8" x 3/8. Cole Parmer Cat. No. EW-04158-10. About 2.37kg (750 pieces) of the grinding media were used per milling jar.
Sieve: USA standard test sieve, No 10. (2mm). Stainless steel frame and wire, 8" diameter. Cole Parmer Cat. No. EW-59984-01.

### Approach

The chemical precursors were first evaluated to determine the molar amount of metal per unit weight of precursor. The established molar quantities were then used to determine the precursor quantities yielding the desired metal ratio. The respective precurors were weighed and mixed, calcined, and finally milled following the methods prescribed in the Kamauchi patent. The synthesized materials were analyzed for phase content by X-ray diffraction and particle size by several methods.

## RESULTS AND DISCUSSION

### Precursor Analysis

The cobalt (II) carbonate hydrated as purchased contains unknown amount of hydrated water. It is necessary to determine the water content in order to achieve an accurate stoichiometry.

Before the analysis, it is necessary to allow the cobalt (II) carbonate sample to reach equilibrium with normal lab atmosphere so that no water will be gained or lost during sample handling. To achieve this, about 20 g of cobalt (II) carbonate was placed on a dish and exposed to normal lab atmosphere for 14 hours. Then the exposed cobalt (II) carbonate was analyzed with TGA (thermogravimetric analyzer) to determine the water content from the weight loss. The TGA ramp rate was 10C/min. The atmosphere was 4% $H_2$ in $N_2$. The result is shown in Figure 1.

Figure 1. TGA Curve of Cobalt (II) Carbonate Hydrated
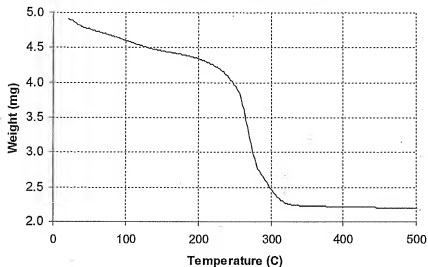


The total wt loss from room temp to 500C was about 54.8%, corresponding to $CoCO_3$ 8.0 $H_2O$ (MW= 262.9). The amount of water in excess of the amount corresponding to the known hexa-hydrated form (see, for example "Merck Index") is probably due to absorbed water. Since water of hydration does not form with $Li_2CO_3$ or FeO, and the P precursor was in liquid form, this analysis was not required to generate the necessary molar quantities of lithium, iron, or phosphorous per gram of their respective precursors.

**Synthesis of materials**
The respective precursor chemicals were used for the synthesis of Li-Co-$PO_4$ and LiFe$PO_4$ according to the teachings of the Kamauchi patent. Note that the precursor mixing method used in this experiment, grinding in a mortar and pestle, is more detailed and thorough than that described in the Kamauchi patent (see Appendix A). The mortar and pestle mixing employed in this experiment tends to reduce precursor particle size. Therefore, this approach will help minimize product particle size thus making the experiment more favorable towards achieving the results asserted in the Kamauchi patent.

Synthesis of Li-Co-$PO_4$ mixed-phase material
According to the Kamauchi patent, it is understood that the product, hereafter referred to as Li-Co-$PO_4$ positive electrode material mix, is not a pure phase, but is a mixture of lithium phosphate, lithium cobalt phosphate, and lithium cobalt oxide. The amounts of

starting materials actually used in this experiment are shown in Table 1 and yielded a Li:Co:P atomic (mole) ratio of 2:1:1. The atomic ratio used matches that used in Example 1 of the Kamauchi patent (Appendix A).

Table 1. Amounts of Starting Materials for the Synthesis of
         Li-Co-PO₄ Material Mix

| Materials | Molar mass | Wt (g) used | Moles | Atomic ratio |
|---|---|---|---|---|
| $Li_2CO_3$ | 73.88 | 4.984 | 0.06746 | 2.00 |
| $CoCO_3$ 8.0 $H_2O$ | 262.9 | 17.75 | 0.06752 | 1.00 |
| $H_3PO_4$, 85% solution | 98.00 | 7.785 | 0.06752 | 1.00 |

$Li_2CO_3$ and $CoCO_3$ 8.0 $H_2O$ were weighed out and mixed with mortar and pestle for about 10 minutes. After grinding, the color was uniformly pink. Then phosphoric acid was added and mixing continued for another 20 minutes. Within a few minutes after adding phosphoric acid, foaming due to generation of $CO_2$ was observed. After the mixing, the power appeared dry. The color was pink.

The mix was then placed in a crucible and heated in the furnace. The temperature was ramped up at 10 C/min to 900 C, then held at 900 C for 24 hours. The weight of the reaction mix before heating was 29.535g. The weight of the product mix after heating was 17.382g. After heating, the product was in the form of a soft cake of powder. The color of the product was dark gray. The product was later ground and milled, as described below.

Synthesis of LiFePO₄ material
According to a journal article (Padhi, 1997, see Appendix B), the mole ratio of Li, Fe and P should be 1:1:1. The amounts of starting materials actually used in this experiment for the synthesis of LiFePO₄ are shown in Table 2.

Table 2. Amount of Starting Materials for the Synthesis of LiFePO₄

| Materials | Molar mass | Wt (g) used | Moles | Atomic ratio |
|---|---|---|---|---|
| $Li_2CO_3$ | 73.88 | 4.889 | 0.06617 | 1.00 |
| FeO | 71.85 | 9.511 | 0.13237 | 1.00 |
| $H_3PO_4$, 85% solution | 98 | 15.31 | 0.1328 | 1.00 |

$Li_2CO_3$ and FeO were first weighed out and ground together with mortar and pestle for 20 minutes. After grinding, the color was uniformly gray. Then $H_3PO_4$ was added. Gas (presumably $CO_2$) was generated. After mixing of the above material, the material was dark gray and mud-like. The material was heated under nitrogen at 300°C for one hour. After heating, the material forms brittle lumps. The color was not uniform, from light gray to dark gray. The material was then ground with a mortar and pestle. Then the material was further heated under nitrogen at 800°C for 24 hours. After heating, the product was in the form of a sintered hard cake. The product color was not uniform,

from gray to beige. Some of the material adhered to the crucible tightly and could not be collected. The product was also later ground and milled, as described below.

**Grinding of materials**
The Li-Co-PO$_4$ positive electrode material mix and the LiFePO$_4$ were ground using the same method but in two separated jars. The method used followed the teachings of Examples 10, 11, and 12 from the Kamauchi patent. The grinding jar was charged with 2.37kg (750 pieces) of grinding media. The material to be ground was added to the jar. In the case of LiCoPO$_4$, the soft cake of material from the heating was crushed by hand and added to the milling jar. In the case of LiFePO$_4$, the hard cake of material from the heating was crushed with mortar and pestle until the particle size was less than about 1mm, then added to the milling mar. The jar mill was turned on and adjusted to 150+/-7 rpm. After 24 hours of grinding, the powder was separated from the grinding media with a coarse (2mm) sieve. After grinding, the color of the Li-Co-PO$_4$ positive electrode material mix powder was dark gray. The color of the LiFePO$_4$ powder was grayish beige.

Phase Analysis via X-ray diffraction
X-ray diffraction measurements were performed on the synthesized and ground materials. The X-ray diffraction patterns are shown in Figures 2 and 3. The pattern of the Li-Co-PO$_4$ material mix did not match that of LiCoPO$_4$ from literature. This was expected since it was a mixture. The pattern of the LiFePO$_4$ material matched XRD patterns for LiFePO$_4$ in the literature (stick pattern shown by black lines in Figure 3), but some impurity phases could be seen.

Figure 2. X-ray Diffraction Pattern of Li-Co-PO$_4$ Mixed Phase Material
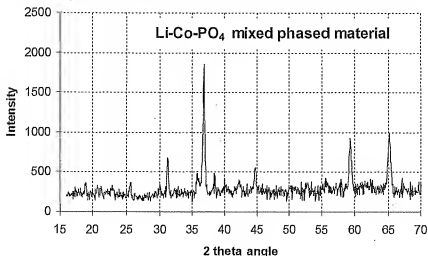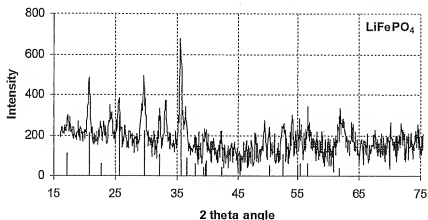
Figure 3. X-ray Diffraction Pattern of LiFePO$_4$ Material



**Particle size analysis**
Attempts were made to measure the particle size distribution with the Malvern Zetasizer ZEN3600 particle size analyzer. Approximately 0.1 g of the Li-Co-PO$_4$ mixed phase sample after 24 hour grinding was added to 20 mL of water. The mix was shaken by hand for 1 minute and sonicated in an ultrasonic bath for 30 minutes. However, during the duration (about 2 minutes) of analysis, a significant portion of the sample precipitated. The Malvern Zetasizer ZEN3600 particle size analyzer is designed for particles small enough not to precipitate out during measurement even without stirring. The fact that Li-Co-PO$_4$ mixed phase powder precipitated indicated that the particles were too large for the instrument. Because of this difficulty, samples of both the Li-Co-PO$_4$ mixed phase powder and LiFePO$_4$ powder were sent to Micromeritics Analytical Services[1] for particle size analysis by a light scattering technique performed with a Micromeritics Saturn DigiSizer 5200 Particle size analyzer (which has a larger maximum size range than the ZEN3600). General descriptions of the analysis techniques available at Micromeritics are given in Appendix C. Standard method 520-01 (non-aqueous liquid dispersion) was chosen as the method. Isopropanol was chosen as the liquid for two reasons: (1) Isopropanol wets the samples very well. (2) All components, including possible impurities, in the samples are expected to be insoluble in isopropanol.

In the preparation of the dispersion, 2.2g of the sample was added to 80 mL of isopropanol. The dispersion was sonicated using a high intensity (100 W) ultrasonic probe for one minute in order to break any agglomerates of particles. An ultrasonic probe (instead of an ultrasonic bath) was used because of its much higher intensity. The analysis was done twice for each sample. The results reported here are the average of the two analyses. The particle size distribution can be shown as a <u>volume distribution</u>, or as a <u>number distribution</u>. The difference and relationship between the two is explained in Appendix D. The NanoGram patent application describes particle size distributions with

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[1] Micromeritics Analytical Services, www.particletesting.com, One Micromeritics Drive, Norcross, Georgia 30093-1877. (770)772-3630

respect to a number distribution. However, it is also common to describe a particle size distribution with respect to volume distribution. Therefore, the data in this experiment is provided both ways. For the two samples, the particle size volume distributions are shown graphically in Figures 4 and 5. The particle size number distributions are shown graphically in Figures 6 and 7. The numerical values of cumulative volume fraction are shown in Tables 3 and 4.

Figure 4. Particle Size **Volume** Distribution of Li-Co-PO$_4$ Mixed-Phase Material
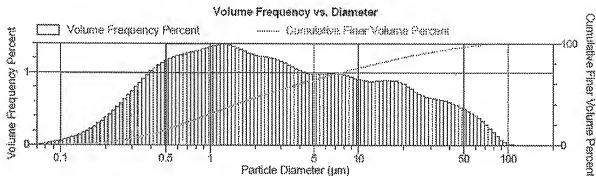


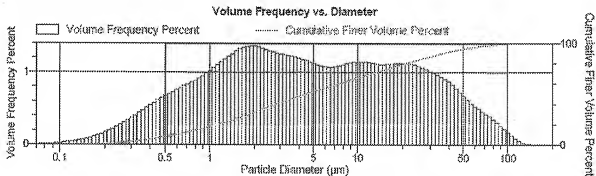Figure 5. Particle Size **Volume** Distribution of LiFePO$_4$ Material

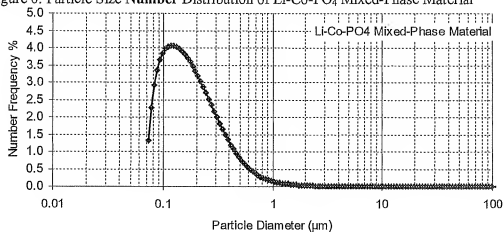Figure 6. Particle Size **Number** Distribution of Li-Co-PO$_4$ Mixed-Phase Material



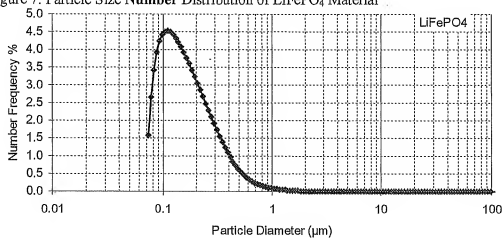Figure 7. Particle Size **Number** Distribution of LiFePO$_4$ Material

Table 3.  Cumulative **Volume** Fractions of Li-Co-PO$_4$ Mixed-Phase Material
Smaller than a Particular Particle Size from Two Separate Measurement Runs.

| Particle size (diameter in µm) | % volume smaller than particle size | | | | Particle size (diameter in µm) | % volume smaller than particle size | | | |
|---|---|---|---|---|---|---|---|---|---|
| | Test 1 | Test 2 | Average | Standard Deviation | | Test 1 | Test 2 | Average | Standard Deviation |
| 0.073 | 0.00% | 0.00% | 0.00% | 0.00% | 3.668 | 45.95% | 46.08% | 46.02% | 0.09% |
| 0.082 | 0.01% | 0.01% | 0.01% | 0.00% | 4.116 | 48.38% | 48.48% | 48.43% | 0.07% |
| 0.092 | 0.02% | 0.04% | 0.03% | 0.01% | 4.618 | 50.72% | 50.82% | 50.77% | 0.07% |
| 0.103 | 0.05% | 0.08% | 0.07% | 0.02% | 5.182 | 52.98% | 53.08% | 53.03% | 0.07% |
| 0.116 | 0.10% | 0.15% | 0.12% | 0.04% | 5.814 | 55.17% | 55.27% | 55.22% | 0.07% |
| 0.130 | 0.17% | 0.25% | 0.21% | 0.05% | 6.523 | 57.32% | 57.42% | 57.37% | 0.07% |
| 0.146 | 0.28% | 0.38% | 0.33% | 0.07% | 7.319 | 59.49% | 59.58% | 59.53% | 0.06% |
| 0.164 | 0.43% | 0.56% | 0.50% | 0.09% | 8.213 | 61.72% | 61.77% | 61.75% | 0.04% |
| 0.184 | 0.65% | 0.80% | 0.73% | 0.11% | 9.215 | 64.01% | 64.02% | 64.02% | 0.01% |
| 0.206 | 0.95% | 1.12% | 1.04% | 0.12% | 10.339 | 66.31% | 66.31% | 66.31% | 0.00% |
| 0.231 | 1.35% | 1.54% | 1.44% | 0.13% | 11.600 | 68.59% | 68.59% | 68.59% | 0.00% |
| 0.260 | 1.86% | 2.06% | 1.96% | 0.14% | 13.016 | 70.82% | 70.84% | 70.83% | 0.02% |
| 0.291 | 2.51% | 2.70% | 2.61% | 0.14% | 14.604 | 73.03% | 73.06% | 73.04% | 0.02% |
| 0.327 | 3.30% | 3.48% | 3.39% | 0.13% | 16.386 | 75.25% | 75.27% | 75.26% | 0.02% |
| 0.367 | 4.23% | 4.40% | 4.32% | 0.12% | 18.386 | 77.50% | 77.50% | 77.50% | 0.00% |
| 0.412 | 5.31% | 5.46% | 5.38% | 0.11% | 20.629 | 79.76% | 79.74% | 79.75% | 0.01% |
| 0.462 | 6.52% | 6.65% | 6.59% | 0.10% | 23.146 | 82.00% | 81.98% | 81.99% | 0.01% |
| 0.518 | 7.85% | 7.98% | 7.91% | 0.09% | 25.970 | 84.18% | 84.16% | 84.17% | 0.01% |
| 0.581 | 9.28% | 9.41% | 9.35% | 0.09% | 29.139 | 86.27% | 86.26% | 86.27% | 0.01% |
| 0.652 | 10.81% | 10.95% | 10.88% | 0.10% | 32.695 | 88.27% | 88.26% | 88.27% | 0.01% |
| 0.732 | 12.43% | 12.60% | 12.52% | 0.12% | 36.684 | 90.19% | 90.17% | 90.18% | 0.01% |
| 0.821 | 14.16% | 14.35% | 14.26% | 0.13% | 41.160 | 91.98% | 91.95% | 91.96% | 0.02% |
| 0.921 | 16.01% | 16.22% | 16.12% | 0.15% | 46.182 | 93.58% | 93.55% | 93.56% | 0.03% |
| 1.034 | 18.01% | 18.23% | 18.12% | 0.15% | 51.817 | 94.96% | 94.94% | 94.95% | 0.02% |
| 1.160 | 20.17% | 20.38% | 20.27% | 0.15% | 58.140 | 96.12% | 96.13% | 96.12% | 0.01% |
| 1.302 | 22.48% | 22.70% | 22.59% | 0.15% | 65.234 | 97.08% | 97.15% | 97.11% | 0.05% |
| 1.460 | 24.95% | 25.18% | 25.06% | 0.17% | 73.194 | 97.89% | 98.03% | 97.96% | 0.10% |
| 1.639 | 27.53% | 27.80% | 27.66% | 0.19% | 82.125 | 98.57% | 98.76% | 98.67% | 0.13% |
| 1.839 | 30.19% | 30.51% | 30.35% | 0.22% | 92.146 | 99.13% | 99.33% | 99.23% | 0.14% |
| 2.063 | 32.89% | 33.25% | 33.07% | 0.25% | 103.389 | 99.54% | 99.71% | 99.63% | 0.12% |
| 2.315 | 35.59% | 35.95% | 35.77% | 0.25% | 116.005 | 99.82% | 99.92% | 99.87% | 0.07% |
| 2.597 | 38.26% | 38.57% | 38.41% | 0.22% | 130.159 | 99.95% | 99.99% | 99.97% | 0.03% |
| 2.914 | 40.88% | 41.12% | 41.00% | 0.17% | 146.041 | 100.00% | 100.00% | 100.00% | 0.00% |
| 3.269 | 43.45% | 43.62% | 43.53% | 0.12% | | | | | |

From the table, for example, only 0.07% of the volume of the powder is in particles smaller than 0.103µm, 1.04% smaller than 0.206µm, 7.91% smaller than 0.518µm, 18.12% smaller than 1.034µm, and 33.07% smaller than 2.063µm. The reproducibility of the two tests were excellent, as indicated by the small standard deviation.

Table 4. Cumulative **Volume** Fractions of LiFePO$_4$ Material Smaller than a Particular
Particle Size from Two Separate Measurement Runs.

| Particle size (diameter in µm) | % volume smaller than particle size | | | | Particle size (diameter in µm) | % volume smaller than particle size | | | |
|---|---|---|---|---|---|---|---|---|---|
| | Test 1 | Test 2 | Average | Standard deviation | | Test 1 | Test 2 | Average | Standard deviation |
| 0.073 | 0.00% | 0.00% | 0.00% | 0.00% | 2.914 | 54.18% | 54.23% | 54.21% | 0.04% |
| 0.082 | 0.03% | 0.03% | 0.03% | 0.00% | 3.269 | 56.48% | 56.51% | 56.50% | 0.02% |
| 0.092 | 0.09% | 0.10% | 0.09% | 0.01% | 3.668 | 58.67% | 58.69% | 58.68% | 0.02% |
| 0.103 | 0.19% | 0.22% | 0.20% | 0.02% | 4.116 | 60.74% | 60.77% | 60.76% | 0.02% |
| 0.116 | 0.35% | 0.39% | 0.37% | 0.03% | 4.618 | 62.74% | 62.77% | 62.75% | 0.02% |
| 0.130 | 0.57% | 0.62% | 0.60% | 0.04% | 5.182 | 64.69% | 64.72% | 64.71% | 0.02% |
| 0.146 | 0.88% | 0.95% | 0.91% | 0.05% | 5.814 | 66.64% | 66.67% | 66.66% | 0.03% |
| 0.164 | 1.29% | 1.37% | 1.33% | 0.06% | 6.523 | 68.59% | 68.64% | 68.62% | 0.04% |
| 0.184 | 1.83% | 1.93% | 1.88% | 0.07% | 7.319 | 70.54% | 70.62% | 70.58% | 0.06% |
| 0.206 | 2.52% | 2.64% | 2.58% | 0.08% | 8.213 | 72.47% | 72.57% | 72.52% | 0.07% |
| 0.231 | 3.40% | 3.53% | 3.47% | 0.09% | 9.215 | 74.36% | 74.46% | 74.41% | 0.07% |
| 0.260 | 4.49% | 4.62% | 4.56% | 0.09% | 10.339 | 76.21% | 76.28% | 76.24% | 0.05% |
| 0.291 | 5.80% | 5.94% | 5.87% | 0.09% | 11.600 | 78.02% | 78.05% | 78.04% | 0.02% |
| 0.327 | 7.35% | 7.48% | 7.42% | 0.09% | 13.016 | 79.81% | 79.81% | 79.81% | 0.00% |
| 0.367 | 9.14% | 9.25% | 9.19% | 0.08% | 14.604 | 81.60% | 81.58% | 81.59% | 0.01% |
| 0.412 | 11.13% | 11.23% | 11.18% | 0.07% | 16.386 | 83.38% | 83.37% | 83.37% | 0.01% |
| 0.462 | 13.30% | 13.39% | 13.34% | 0.06% | 18.386 | 85.12% | 85.14% | 85.13% | 0.01% |
| 0.518 | 15.61% | 15.69% | 15.65% | 0.06% | 20.629 | 86.80% | 86.84% | 86.82% | 0.03% |
| 0.581 | 18.02% | 18.10% | 18.06% | 0.05% | 23.146 | 88.37% | 88.42% | 88.40% | 0.03% |
| 0.652 | 20.50% | 20.58% | 20.54% | 0.06% | 25.970 | 89.83% | 89.85% | 89.84% | 0.02% |
| 0.732 | 23.02% | 23.11% | 23.07% | 0.06% | 29.139 | 91.19% | 91.19% | 91.19% | 0.00% |
| 0.821 | 25.59% | 25.69% | 25.64% | 0.07% | 32.695 | 92.50% | 92.48% | 92.49% | 0.02% |
| 0.921 | 28.22% | 28.33% | 28.28% | 0.08% | 36.684 | 93.77% | 93.73% | 93.75% | 0.03% |
| 1.034 | 30.92% | 31.03% | 30.97% | 0.08% | 41.160 | 94.95% | 94.93% | 94.94% | 0.02% |
| 1.160 | 33.67% | 33.78% | 33.72% | 0.08% | 46.182 | 96.04% | 96.04% | 96.04% | 0.00% |
| 1.302 | 36.45% | 36.55% | 36.50% | 0.07% | 51.817 | 97.01% | 97.05% | 97.03% | 0.03% |
| 1.460 | 39.20% | 39.29% | 39.24% | 0.06% | 58.140 | 97.87% | 97.95% | 97.91% | 0.05% |
| 1.639 | 41.87% | 41.95% | 41.91% | 0.06% | 65.234 | 98.64% | 98.73% | 98.68% | 0.06% |
| 1.839 | 44.43% | 44.51% | 44.47% | 0.06% | 73.194 | 99.26% | 99.34% | 99.30% | 0.06% |
| 2.063 | 46.91% | 47.00% | 46.95% | 0.06% | 82.125 | 99.70% | 99.75% | 99.72% | 0.04% |
| 2.315 | 49.36% | 49.44% | 49.40% | 0.06% | 92.146 | 99.93% | 99.94% | 99.93% | 0.01% |
| 2.597 | 51.80% | 51.87% | 51.83% | 0.05% | 103.389 | 100.00% | 100.00% | 100.00% | 0.00% |
| | | | | | 109.515 | 100.00% | 100.00% | 100.00% | 0.00% |

From the table, for example, only 0.20% of the volume of the powder is in particles
smaller than 0.103µm, 2.58% smaller than 0.206µm, 15.65% smaller than 0.518µm,
30.97% smaller than 1.034µm, and 46.95% smaller than 2.063µm. The reproducibility of
the two tests were excellent, as indicated by the small standard deviation.

Table 5. Cumulative **Number** Fractions of Li-Co-PO$_4$ Mixed-Phase Material
Smaller than a Particular Particle Size from Two Separate Measurement Runs.

| Particle size (diameter in μm) | % number smaller than particle size | Particle size (diameter in μm) | % number smaller than particle size |
|---|---|---|---|
| 0.075 | 1.33% | 0.671 | 97.27% |
| 0.080 | 3.60% | 0.711 | 97.63% |
| 0.085 | 6.52% | 0.753 | 97.95% |
| 0.090 | 9.88% | 0.798 | 98.22% |
| 0.095 | 13.54% | 0.845 | 98.46% |
| 0.100 | 17.39% | 0.895 | 98.67% |
| 0.106 | 21.36% | 0.948 | 98.85% |
| 0.113 | 25.39% | 1.005 | 99.01% |
| 0.119 | 29.44% | 1.064 | 99.15% |
| 0.126 | 33.49% | 1.127 | 99.27% |
| 0.134 | 37.51% | 1.194 | 99.38% |
| 0.142 | 41.48% | 1.265 | 99.47% |
| 0.150 | 45.37% | 1.340 | 99.55% |
| 0.159 | 49.18% | 1.419 | 99.62% |
| 0.169 | 52.89% | 1.503 | 99.68% |
| 0.179 | 56.49% | 1.592 | 99.73% |
| 0.189 | 59.96% | 1.686 | 99.77% |
| 0.200 | 63.29% | 1.786 | 99.81% |
| 0.212 | 66.47% | 1.892 | 99.84% |
| 0.225 | 69.50% | 2.004 | 99.87% |
| 0.238 | 72.36% | 2.123 | 99.89% |
| 0.252 | 75.05% | 2.249 | 99.91% |
| 0.267 | 77.57% | 2.382 | 99.92% |
| 0.283 | 79.91% | 2.523 | 99.94% |
| 0.300 | 82.08% | 2.673 | 99.95% |
| 0.318 | 84.07% | 2.831 | 99.96% |
| 0.336 | 85.89% | 2.999 | 99.96% |
| 0.356 | 87.55% | 3.177 | 99.97% |
| 0.378 | 89.05% | 3.365 | 99.97% |
| 0.400 | 90.39% | 3.564 | 99.98% |
| 0.424 | 91.59% | 3.776 | 99.98% |
| 0.449 | 92.66% | 3.999 | 99.99% |
| 0.475 | 93.61% | 4.236 | 99.99% |
| 0.503 | 94.44% | 4.487 | 99.99% |
| 0.533 | 95.17% | 4.753 | 99.99% |
| 0.565 | 95.81% | 5.035 | 99.99% |
| 0.598 | 96.36% | 5.333 | 99.99% |
| 0.634 | 96.85% | 5.649 | 99.99% |
|  |  | 5.984 | 100.00% |

From the table, for example, only 17.39% of the number of particles are smaller than
0.100μm, and 63.29% smaller than 0.200μm.

Table 6. Cumulative Number Fractions of LiFePO$_4$ Material Smaller than a Particular
Particle Size from Two Separate Measurement Runs.

| Particle size (diameter in μm) | % number smaller than particle size | Particle size (diameter in μm) | % number smaller than particle size |
|---|---|---|---|
| 0.075 | 1.57% | 0.598 | 97.77% |
| 0.080 | 4.24% | 0.634 | 98.11% |
| 0.085 | 7.65% | 0.671 | 98.40% |
| 0.090 | 11.57% | 0.711 | 98.65% |
| 0.095 | 15.79% | 0.753 | 98.86% |
| 0.100 | 20.20% | 0.798 | 99.03% |
| 0.106 | 24.70% | 0.845 | 99.18% |
| 0.113 | 29.22% | 0.895 | 99.31% |
| 0.119 | 33.70% | 0.948 | 99.42% |
| 0.126 | 38.12% | 1.005 | 99.52% |
| 0.134 | 42.45% | 1.064 | 99.59% |
| 0.142 | 46.66% | 1.127 | 99.66% |
| 0.150 | 50.74% | 1.194 | 99.72% |
| 0.159 | 54.67% | 1.265 | 99.77% |
| 0.169 | 58.44% | 1.340 | 99.81% |
| 0.179 | 62.05% | 1.419 | 99.84% |
| 0.189 | 65.47% | 1.503 | 99.87% |
| 0.200 | 68.72% | 1.592 | 99.89% |
| 0.212 | 71.78% | 1.686 | 99.91% |
| 0.225 | 74.65% | 1.786 | 99.92% |
| 0.238 | 77.32% | 1.892 | 99.94% |
| 0.252 | 79.80% | 2.004 | 99.95% |
| 0.267 | 82.10% | 2.123 | 99.96% |
| 0.283 | 84.20% | 2.249 | 99.96% |
| 0.300 | 86.11% | 2.382 | 99.97% |
| 0.318 | 87.85% | 2.523 | 99.97% |
| 0.336 | 89.42% | 2.673 | 99.98% |
| 0.356 | 90.82% | 2.831 | 99.98% |
| 0.378 | 92.06% | 2.999 | 99.99% |
| 0.400 | 93.17% | 3.177 | 99.99% |
| 0.424 | 94.14% | 3.365 | 99.99% |
| 0.449 | 94.98% | 3.564 | 99.99% |
| 0.475 | 95.72% | 3.776 | 99.99% |
| 0.503 | 96.36% | 3.999 | 99.99% |
| 0.533 | 96.90% | 4.236 | 100.00% |
| 0.565 | 97.37% | | |

From the table, for example, only 20.20% of the number of particles are smaller than
0.100μm, and 68.72% smaller than 0.200μm.

## CONCLUSIONS

In this experiment, Li-Co-PO$_4$ mixed-phase material were synthesized using methods taught in United States Patent #5,538,714 (the "Kamauchi Patent"), and and LiFePO$_4$ material was synthesized using the approaches of the Goodenough research group. Both materials were ground using the method in the Kamauchi Patent. After grinding, both powders were analyzed for particle size distribution. The results clearly indicated that the particles have a broad particle size distribution.

## APPENDIX

### A: US patent 5,538,814 - Lithium Secondary Batteries, Kamauchi et al.

For reference, the relevant parts of US Patent # 5,538,814 (the Kamauchi patent) are highlighted below

Example 1
Predetermined amounts of lithium carbonate, basic cobalt carbonate, and 85% phosphoric acid aqueous solution were weighed to fulfill an atomic ratio of Li:Co:P=2:1:1, sufficiently mixed in an alumina crucible, and heated at 900° C in an electric oven for twenty-four hours.
The heated product was identified by X-ray powder diffraction analysis with the use of JCPDS cards. The results of the X-ray analysis showed that the product contained lithium phosphate, lithium-cobalt phosphate, and cobalt oxide at a molar ratio of Li:Co:P=1:0.5:0.5

Example 10
The positive electrode active material obtained in Example 1 was further pulverized in a ball mill for 24 hours to adjust the average particle size thereof to about 0.5 um, and the BET specific surface area to 5 m$^2$/g.
Twenty lithium batteries were fabricated in the same manner as in Example 1 by using this positive electrode.

Examples 11, 12
In the same manner as in Example 10 except that the average particle size, and the BET specific surface area of the positive electrode active material were changed as shown in Table 3 by varying the pulverizing time in a ball mill, 20 lithium batteries were fabricated in each Example.
The lithium batteries of Example 10-12 were charged in the same manner as above, and discharge capacity was determined, the results of which are shown in Table 7 wherein the figures are average values.

Partial Table 7

| | Active material average particle size (μm) | BET specific surface area (m²/g) |
|---|---|---|
| Example 10 | 0.5 | 5 |
| Example 11 | 5 | 1 |
| Example 12 | 0.01 | 800 |

**B. Padhi (1997) article on Phospho-olivines**
The original publication on the use of $LiFePO_4$ for lithium secondary batteries is
"Phospho-olivines as Positive-Electrode Materials for Rechargeable Lithium Batteries",
by A. K. Padhi, K. S. Nanjundaswamy, and J. B. Goodenough,
Journal of The Electrochemical Society, Vol. 144, issue 4, page 1188-1193 (1997). A
copy of this article is attached. For completeness, the most relevant parts of the article
are highlighted below.

Experimental
$LiMPO_4$ (M = Mn, Fe, Co, or Ni) compounds were prepared by direct solid-state reaction
of stoichiometric amounts of M(II)-acetates, ammonium phosphate, and lithium
carbonate. $LiFePO4$ and $LiFe_{1-x}Mn_xP0_4$ (x = 0.25, 0.50, and 0.75) were synthesized in
inert atmosphere to prevent the formation of $Fe^{3+}$ compounds as impurities. The
intimately ground stoichiometric mixture of the starting materials was first decomposed
at 300 to 350°C to drive away the gases. The mixture was then reground and returned to
the furnace at 800°C for 24 h before being cooled slowly to room temperature.

**C. Particle Size Analysis by Laser Light Scattering conducted a Micromeritics**
Laser light scattering technique utilizes Mie and Fraunhofer Theories to determine
particle size distribution from a light scattering pattern. Micromeritics has both the Saturn
Digisizer 5200 and the Mastersizer 2000 available for this technique. The Mastersizer
2000 is capable of performing particle size distribution using either the dry dispersion
module or wet dispersion module. The Saturn Digisizer 5200 is the highest resolution
instrument available, capable of distinguishing small differences in samples. The particle
size range is 0.02 μm to 2000 μm.
Available standard tests:
520 - 00
Particle size analysis using an aqueous dispersion. A distribution of particle size diameter
is reported between 0.1 to 1000 micrometers. The technique requires at least 2 grams of
dry sample material.

520 - 01
Particle size analysis using a non-aqueous dispersion. A distribution of particle size
diameter is reported between 0.1 to 1000 micrometers. The technique requires at least 2
grams of dry sample material.

## D. Relationship between volume distribution and number distribution

The result of particle size analysis is expressed as a distribution, which states what percentage of the powder sample is in each size range. If the percentage is based on volume of particles, the distribution is a volume distribution. Alternatively, if the percentage is based on number of particles, the distribution is a number distribution. The relationship between the two distributions is illustrated a very simple example. Assuming there are 4 particles with diameter 1$\mu$m, 3 particles with diameter 2$\mu$m, 2 particles with diameter 3$\mu$m, and 1 particle with diameter 4$\mu$m. The volume distribution and the number distribution are calculated in the table below, and shown in the figure below.

| Particle Diameter | Number of particles | % of number of particles with that diameter | Vol of each particle | Sum of Vol of particles with that diameter | % of Vol of particles with that diameter |
|---|---|---|---|---|---|
| 1 | 4 | 40% | 0.524 | 2.09 | 3% |
| 2 | 3 | 30% | 4.189 | 12.57 | 16% |
| 3 | 2 | 20% | 14.137 | 28.27 | 37% |
| 4 | 1 | 10% | 33.510 | 33.51 | 44% |
| Sum of all particles | 10 | | | 76.45 | |
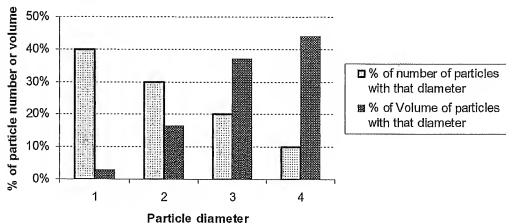


From the example above, it can be understood that number distribution tends to show higher % for smaller particles, and volume distribution tends to show higher % for larger particles. Based on an assumption of uniform particle shape, each distribution can be converted from one representation to the other. As presented above, the particles were assumed to be spherical.